END
DATE
FILMED

8 80

DTIC

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

ADA086239

LEVEL

THE MOLYBDENUM-MOLYBDENUM TRIPLE BOND. 7.[1]

BIS(1,3-Di-p-TOLYLTRIAZENIDO)TETRAKIS(DIMETHYLAMIDO)DIMOLYBDENUM

by

M. H. Chisholm, D. A. Haitko, J. C. Huffman and K. Folting

Prepared for Publication

in

Inorganic Chemistry

DTIC
SELECTE
JUL 7 1980
C

Department of Chemistry
Indiana University
Bloomington, Indiana 47405

9 May 80

DDC FILE COPY

80 7 3 118

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A086 239	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Molybdenum-Molybdenum Triple Bond. 7.[1] Bis(1,3-Di-p-tolyltriazenido)tetrakis(dimethylamido)dimolybdenum.		5. TYPE OF REPORT & PERIOD COVERED Technical Report 1980
		6. PERFORMING ORG. REPORT NUMBER TR-80-1
7. AUTHOR(s) M. H. Chisholm, D. A. Haitko, J. C. Huffman and K. Folting		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0826
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Indiana University Bloomington, Indiana 47405		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy		12. REPORT DATE May 9, 1980
		13. NUMBER OF PAGES 14
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release: distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Metal-to-Metal Triple Bonds, Molybdenum, Dimethylamido, Triazenido

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

$Mo_2(NMe_2)_6$ reacts in hydrocarbon solvents with 1,3-di-p-tolyltriazine, $C_7H_8NNNHC_7H_8$, to give the title compound, $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$, as a red, crystalline solid. An X-ray study shows that in the solid state each molybdenum atom is coordinated to four nitrogen atoms which lie in a plane; there is an unbridged molybdenum-to-molybdenum triple bond with a Mo-Mo distance of 2.212(1) Å, and the molecule has crystallographically

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73
S/N 0102-014-6601

imposed C_2 symmetry. Variable temperature ^1H nmr spectra recorded at 220 MHz support the view that this form of the molecule is present in solution. These observations are compared with other findings in dimolybdenum and ditungsten chemistry. Crystal data for $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$ are $a = 27.529(7)$, $b = 8.728(2)$, $c = 18.294(4)$ Å, $\beta = 58.34(1)°$, $V = 3741.58$ Å^3, $Z = 4$, $d_{calcd} = 1.45$ g cm^{-3} and space group $C\,2/c$.

Accession For

NTIS GRA&I

DDC TAB

Unannounced

Justification

By

Distribution/

Availability Codes

Avail and/or

special

Dist

A

Introduction

Previously we have shown that 1,3-diphenyltriazine and $W_2(NMe_2)_6$ react to give $W_2(NMe_2)_4(PhN_3Ph)_2$[2] and $Mo_2(NMe_2)_6$ and 2-hydroxy-6-methylpyridine react to give $Mo_2(NMe_2)_4(C_6H_6NO)_2$.[1] In both reactions, the replacement of two dimethylamido groups is accomplished by an increase in coordination number of the metal, since the triazenide and pyradone ligands act as bidentate ligands. However, the molybdenum and tungsten compounds adopt bridged and unbridged structures, respectively, as shown in 1 and 2 below.
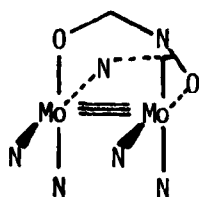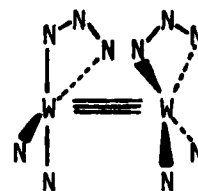
1   2

The preference for the bridged or non-bridged structure could be determined by the subtle differences that exist within the coordination chemistry of molybdenum and tungsten. For example, in closely related compounds containing metal-to-metal triple bonds, the Mo-to-Mo distance is shorter by ca. 0.08 Å than the W-to-W distance and the triazenido ligand is known to bridge the molybdenum-to-molybdenum quadruple bond in the compound $Mo_2(PhN_3Ph)_4$ which has a Mo-to-Mo distance of 2.083(2) Å.[3] As part of our continuing program which is aimed at establishing the coordination chemistry surrounding the $(M \equiv M)^{6+}$ moiety (M = Mo, W), we decided to prepare and structurally characterize the related pair of molybdenum and tungsten compounds. We report here the preparation and characterization of $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$.

Results

Synthesis. In hydrocarbon solvents, $Mo_2(NMe_2)_6$ and 1,3-di-p-tolyltriazine react upon mixing at room temperature to give deep red solutions from which $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$ can be obtained as red crystals from toluene-hexane solvent mixtures. The physical properties are analogous to those reported for the tungsten analog.[2] Analytical data and other spectroscopic data are recorded in the experimental section.

Solid-State Structure. In the crystalline state, the compound is composed of descrete molecules of $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)$. An ORTEP view of the molecule looking down the C_2 axis of symmetry is shown in Figure 1 and the atomic numbering scheme is shown in Figure 2. Final atomic coordinates and thermal parameters are given in Tables 1 and 2. Complete listings of bond distances and angles are given in Tables 3 and 4, respectively. Tables listing a number of least squares planes calculated for this molecule and the deviations of atoms from these planes, together with dihedral angles between planes, are available as supplementary material.

Discussion

The molecule is in every way structurally akin to its tungsten analog. The X-ray data for the molybdenum compound are superior and reveal certain trends which were alluded to in the tungsten structure. For example, there are short (1.943(3) Å) and long (1.970(3) Å) Mo-N bond distances associated with the two types of Mo-NMe$_2$ groups and these are, respectively, trans to long (2.271(3) Å) and short (2.231(3) Å) Mo-N distances of the triazenido ligand.

The Mo-Mo distance is 2.212(1) Å which is slightly shorter than the average of the two crystallographically independent Mo-Mo distances found for $Mo_2(NMe_2)_6$ which were 2.211(2) and 2.217(2) Å.[4] By contrast, the W-W distance in $W_2(NMe_2)_4(PhN_3Ph)_2$ is 2.314(1) Å which is longer than the three crystallographically independent W-W distances found for the $W_2(NMe_2)_6$ molecule.[5] These were 2.294(1) Å found for the $W_2(NMe_2)_6$ molecule which co-crystallized with $W(NMe_2)_6$ and 2.290(2) and 2.294(2) Å found in crystals of pure $W_2(NMe_2)_6$.

For a closely related series of compounds containing the central $(M \equiv M)^{6+}$ unit, we have found that the W-W distance is longer by 0.08 Å than the Mo-Mo distance.[6] Here the distances differ by 0.10 Å which is a small but crystallographically significant deviation from what we expected. However, little chemical significance can be attached to this observation and the bonding in $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$ may be viewed as previously described for the tungsten dimer.

Variable temperature ^{1}H nmr studies reveal the two types of Mo-NMe_2 groups with quite different energies of activation for proximal $\rightleftharpoons$ distal methyl exchange. There are two tolyl-methyl signals, consistent with the maintenance of the C_2 axis of symmetry in solution. Thus, the triazenido moiety is rigidly bound on the nmr time scale. The ^{1}H nmr data do not allow one to distinguish between a bridged structure akin to 1 or the non-bridged structure 2. However, only one isomer is present in solution (one pair of enantiomers, to be precise) and so one can rule out a rapid equilibrium between bridged and non-bridged structures, since this would cause the tolyl-methyl groups to become equivalent on the nmr time scale. Thus, we are inclined to the view that the structure found in the solid state is maintained in solution.

This raises the question: Why does the 2-oxy-6-methylpyridine ligand favor a bridged structure, 1, while the 1,3-diaryltriazenido ligands favor the non-bridged structure 2? We propose that the reason rests solely on the relative ordering of steric repulsive interactions within the molecules (1.). The 2-oxy-6-methylpyridine ligand acts as a strong O-donor and a weak N-donor, as evidenced by the short Mo-O (2.08 Å) and long Mo-N (2.31 Å) bond distances. Furthermore, the pyridine nitrogen accommodates a considerable pyramidal distortion in its coordination to molybdenum in the $Mo_2(NMe_2)_4$(2-oxy-6-methyl-pyridine)$_2$ molecule. In this way, the $Mo_2(NMe_2)_4$ portion of the molecule adopts a skew geometry which reduces the unfavorable steric repulsions which otherwise would result from the eclipsed geometry. A $Mo_2(NMe_2)_4(ArN_3Ar)_2$ molecule having two bridging triazenido groups has no inherent asymmetry and would, therefore, favor a more rigorously eclipsed geometry (2.). If the 2-oxy-6-methylpyridine ligand is placed as a bidentate, but non-bridging group such that each MoN_3O moiety is at least roughly planar, then the methyl group of the pyridine ligand is also confined to this plane. This is clearly unfavorable from steric considerations. In the $M_2(NMe_2)_4(ArN_3Ar)_2$ structures, the phenyl groups are free to rotate about the $N-C_{sp^2}$ bonds and may, as they indeed do, orientate the phenyl blades to reduce this steric repulsion in the MoN_4 plane.

While the above arguments offer a qualitative explanation for the choice of bridging versus non-bridging structures, the structural characterization of the $Mo_2(NMe_2)_4$(2-oxy-6-methylpyridine)$_2$ and $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$ molecules provide furthe, support for the view that the favored geometry for d^3-d^3 dimers $L_4M \equiv ML_4$ has the four ligand atoms, which are directly bonded to each metal, in a plane.

Experimental Section

General procedures, including the preparation of $Mo_2(NMe_2)_6$,[4] have been described previously.

Synthesis of $Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$. $Mo_2(NMe_2)_6$ (0.4477 g, 0.98 mmol) and 1,3-di-p-tolyltriazine (0.52 g, 1.96 mmol) were placed in a 100 mL round-bottomed flask. Dry toluene (50 mL) was added yielding a deep-red solution which was stirred at room temperature for 1/2 h. Hexane (10 mL) was added and the flask was placed in the refrigerator at -10°C. Rust-red crystals were obtained. Elemental analyses were eratic and unsatisfactory. I.r. data obtained from Nujol mull using CsI plates, ν in cm^{-1}: 1596 m, 1380 s, 1340 s, 1293 vs, 1272 vs, 1240 s, 1170 w, 1155 w, 1144 m, 1115 w, 1105 w, 1044 m, 950 s, 935 s, 931 s, 820 s, 759 m, 727 m, 652 m, 624 m, 540 m, 503 m, 366 m. [1]H nmr data obtained from toluene-d_8 at 220 MHz and +16°C: δ (NMe-proximal) = 4.45 (broad), 4.28 (sharp), δ (NMe-distal) = 2.09 (broad), 2.53 (sharp); tolylmethyls δ = 2.29 and 2.22; aromatic protons δ = 7.03, 7.24, 7.42 and 7.59 (all doublets with splittings of ca. 7.5 Hz).

X-Ray Structural Determination. A crystal of dimension of 0.08 x 0.11 x 0.34 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off cooling system of the diffractometer.[8] The diffractometer used for data collection was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and mator Picker X-ray generator is interfaced to a TI980 minicomputer, with Slo-Syn stepping motors to drive the angles. Centering is accomplished by using

automated top/bottom - left/right slit assemblies. The minicomputer is interfaced by slow-speed data lines to a CYBER 172-CDC 6600 multimain frame system where all computations are performed.

The cell dimensions obtained from 20 reflections at -17°C with MoKα (λ = 0.71069 Å) were a = 27.529(7), b = 8.728(2), c = 18.294(4) Å, β = 58.34(1)°, V = 3741.58 Å^3, Z = 4, d_{calcd} = 1.45 g cm^{-3}, and space group C 2/c.

A total of 3730 reflections were collected using standard moving-detector techniques with the following values: scan speed = 3 deg min^{-1}, scan width = 2$\overset{o}{+}$ dispersion, single background time at extremes of scan = 5 s, aperture size = 2.5 x 3.5 mm. The limits of data collection were 5° < 2θ < 50°. The number of reflections with F>2.33σ(F) was 2853.

For the final refinement, all non-hydrogen atoms were allowed to vary anisotropically. The hydrogen positional parameters were also varied, while their isotropic thermal parameters were kept fixed.

The structure was solved by direct methods and Patterson techniques and refined by full-matrix least-squares to yield final residues: R(F) = 0.039 and Rw(F) = 0.040. The goodness of fit for the last cycle was 1.01 and the maximum Δ/σ was 0.1.

Supplementary Data Available. A table of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page. The complete structural report, MSC Report 8001, is available upon request in microfiche form only from the Indiana University Chemical Library.

References

1. Part 6, M. H. Chisholm, J. C. Huffman, K. Felting and I. P. Rothwell, Inorg. Chem., submitted for publication.

2. M. H. Chisholm, J. C. Huffman and R. L. Kelly, Inorg. Chem., 18, 3554 (1979).

3. F. A. Cotton, G. W. Rice and J. C. Sekutowski, Inorg. Chem., 18, 1143 (1979).

4. M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive and B. R. Stults, J. Amer. Chem. Soc., 98, 4469 (1976).

5. M. H. Chisholm, F. A. Cotton, M. W. Extine and B. R. Stults, J. Amer. Chem. Soc., 98, 4477 (1976).

6. For a table listing $M \equiv M$ distances, see M. H. Chisholm, Transition Metal Chemistry, 3, 321 (1978).

7. M. H. Chisholm, Faraday Society Symposium, No. 14 (1980).

8. J. C. Huffman, Ph.D. Thesis, Indiana University, Bloomington, Indiana, 1974.
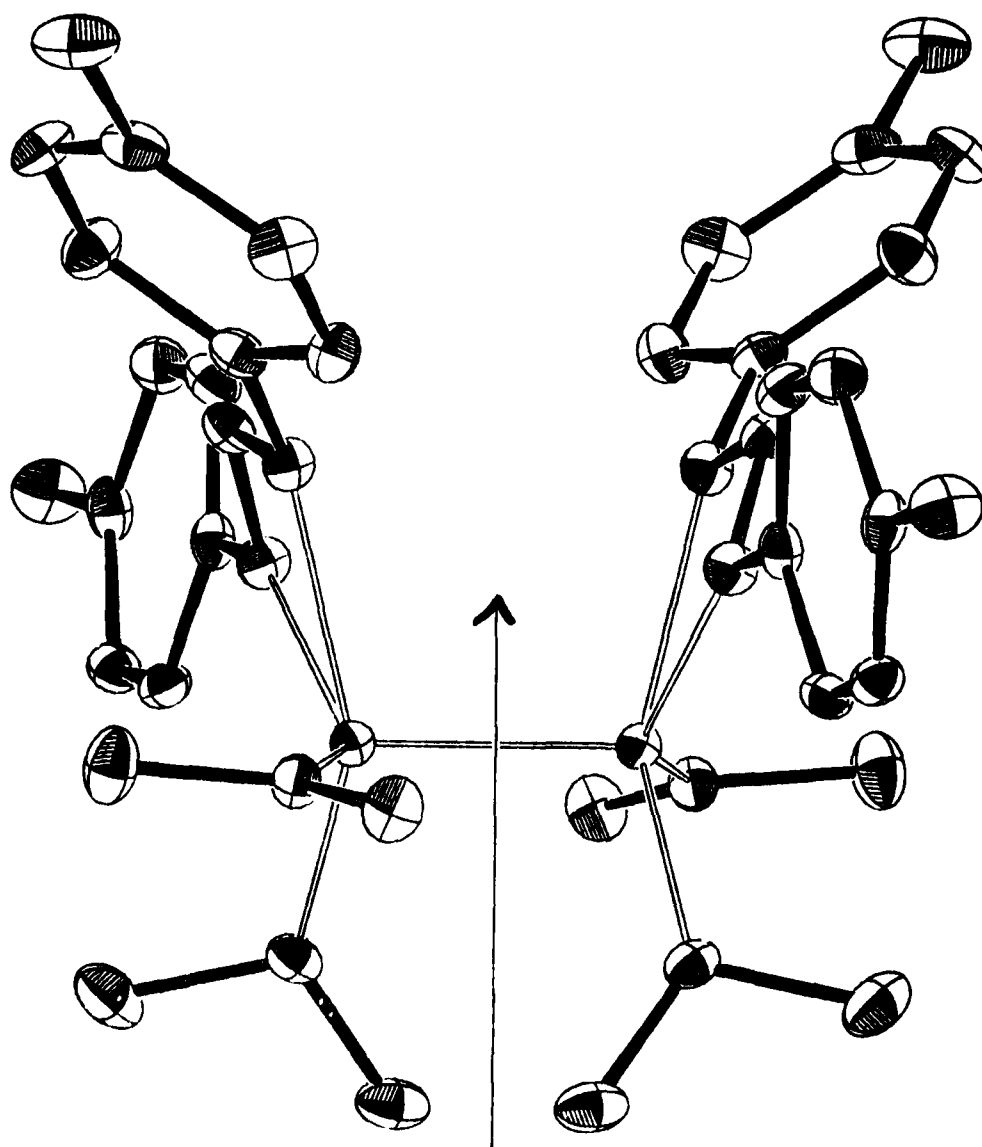
TABLE 3.   Bond Distances, in Angstroms, for the

$Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$ Molecule

A	B	Distance
Mo(1)	Mo(1)'	2.212(1)
Mo(1)	N(2)	2.271(3)
Mo(1)	N(4)	2.231(3)
Mo(1)	N(19)	1.943(3)
Mo(1)	N(22)	1.970(3)
N(2)	N(3)	1.310(4)
N(2)	C(5)	1.431(5)
N(3)	N(4)	1.316(4)
N(4)	C(12)	1.400(5)
N(19)	C(20)	1.459(5)
N(19)	C(21)	1.454(5)
N(22)	C(23)	1.460(5)
N(22)	C(24)	1.449(5)
C(5)	C(6)	1.387(6)
C(5)	C(10)	1.385(5)
C(6)	C(7)	1.388(6)
C(7)	C(8)	1.402(6)
C(8)	C(9)	1.380(6)
C(8)	C(11)	1.507(5)
C(9)	C(10)	1.393(5)
C(12)	C(13)	1.390(6)
C(12)	C(17)	1.394(5)
C(13)	C(14)	1.364(6)
C(14)	C(15)	1.388(6)
C(15)	C(16)	1.397(6)
C(15)	C(18)	1.504(6)
C(16)	C(17)	1.381(6)

TABLE 4. Angles, in Degrees, for the

$Mo_2(NMe_2)_4(C_7H_8N_3C_7H_8)_2$ Molecule

A	B	C	Angle
Mo(1)'	Mo(1)	N(2)	107.8(1)
Mo(1)'	Mo(1)	N(4)	103.1(1)
Mo(1)'	Mo(1)	N(19)	102.6(1)
Mo(1)'	Mo(1)	N(22)	102.6(1)
N(2)	Mo(1)	N(4)	55.8(1)
N(2)	Mo(1)	N(19)	137.0(1)
N(2)	Mo(1)	N(22)	95.9(1)
N(4)	Mo(1)	N(19)	88.4(1)
N(4)	Mo(1)	N(22)	146.5(1)
N(19)	Mo(1)	N(22)	106.3(1)
Mo(1)	N(2)	N(3)	97.4(2)
Mo(1)	N(2)	C(5)	148.2(3)
N(3)	N(2)	C(5)	113.8(3)
N(2)	N(3)	N(4)	106.7(3)
Mo(1)	N(4)	N(3)	99.1(2)
Mo(1)	N(4)	C(12)	138.9(2)
N(3)	N(4)	C(12)	116.6(3)
Mo(1)	N(19)	C(20)	112.6(3)
Mo(1)	N(19)	C(21)	136.5(3)
C(20)	N(19)	C(21)	110.7(3)
Mo(1)	N(22)	C(23)	114.2(3)
Mo(1)	N(22)	C(24)	135.2(3)
C(23)	N(22)	C(24)	110.1(3)
N(2)	C(5)	C(6)	121.9(3)
N(2)	C(5)	C(10)	119.0(3)
C(6)	C(5)	C(10)	119.1(3)
C(5)	C(6)	C(7)	120.0(4)
C(6)	C(7)	C(8)	121.5(4)
C(7)	C(8)	C(9)	117.4(3)
C(7)	C(8)	C(11)	121.3(4)
C(9)	C(8)	C(11)	121.3(4)
C(8)	C(9)	C(10)	121.6(4)
C(5)	C(10)	C(9)	120.3(4)
N(4)	C(12)	C(13)	122.9(3)
N(4)	C(12)	C(17)	118.9(3)
C(13)	C(12)	C(17)	118.2(4)
C(12)	C(13)	C(14)	121.1(4)
C(1.)	C(14)	C(15)	121.8(4)
C(14)	C(15)	C(16)	117.1(4)
C(14)	C(15)	C(18)	121.8(4)
C(16)	C(15)	C(18)	121.1(4)
C(14)	C(16)	C(17)	121.6(4)
C(1.)	C(1.)	C(16)	120.(4)

DATE
FILMED

8-8